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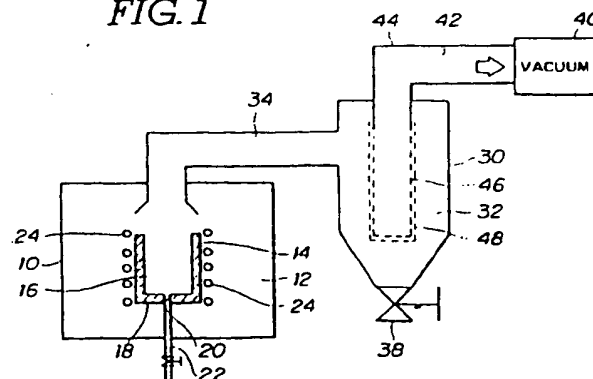
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(54) Method and system for manufacturing fine-grained silicon monoxide.

(57) A method for manufacturing fine-grained SiO powder includes a step of heating a reagent mixture of SiO<sub>2</sub> containing material and Si and/or C containing material for generating SiO vapor, and a step for condensing the generated SiO vapor in gaseous-state under the presence of non-oxidizing gas and under substantially low pressure. Preferably, maintaining the atmosphere pressure at the position where thermal reaction to generate SiO vapor occurs at substantially low pressure, causes flow of the non-oxidizing gas. Such gas flow serves as transfer medium for transferring vapor-state SiO and/or fine-grained SiO powder to a SiO collection chamber. This successfully prevent the SiO from being accumulated within a transfer pipe or duct and thus preventing the pipe or duct from being blocked. Furthermore, substantially low pressure atmosphere encourages SiO vapor generation from the reagent mixture and thus require lower heating temperature to cause SiO vapor generation.

**FIG. 1**



# METHOD AND SYSTEM FOR MANUFACTURING FINE-GRAINED SILICON MONOXIDE

## BACKGROUND OF THE INVENTION

The present invention relates generally to a method and a system for effectively manufacturing fine-grained solid-state silicon monoxide ( $\text{SiO}$ ). More specifically, the invention relates to a method for producing fine  $\text{SiO}$  of grain size less than or equal to  $1\ \mu\text{m}$  in a form of amorphous at substantially high yield and a system for effectively implementing the process of the invention. Further, particularly, the invention relates to a method and a system for producing fine  $\text{SiO}$ , which is industrially applicable.

Fine-grained  $\text{SiO}$  powder is known as very attractive material in the recent fine ceramic industries. For example, such fine-grained  $\text{SiO}$  is known as a material for  $\text{Si}_3\text{N}_4$ ,  $\text{SiC}$  or so forth. Especially, substantially fine-grained  $\text{SiO}$ , such as that have the grain size of less than or equal to  $1\ \mu\text{m}$  is substantially active and thus useful as a material for ceramics.

Japanese Patent Second (examined) Publication (Tokko) Showa 59-50601 discloses a production of fine-grained  $\text{SiO}$  powder. In the disclosed process, a mixture of silicon dioxide ( $\text{SiO}_2$ ) and carbon (C) or  $\text{SiO}_2$  and metallic silicon (Si) is heated at a temperature higher than or equal to  $1500^\circ\text{C}$  under reduced pressure to cause thermal reaction for generating  $\text{SiO}$  vapor. The generated  $\text{SiO}$  vapor is condensed into fine-grained solid-state  $\text{SiO}$  powder of grain size of  $1\ \mu\text{m}$  in amorphous form by causing adiabatic expansion in nitriding or carbonizing reduction atmosphere or pressure-reduced oxygen atmosphere.

Such conventional production process for  $\text{SiO}$  is suitable for producing a small amount of fine  $\text{SiO}$

powder. However, when a large amount of SiO powder has to be produced, the conventional process and the system encounter difficulties. For example, condensation of vapor-state SiO tends to be caused in a transporting duct or pipe for transporting the SiO vapor to a chamber in which adiabatic expansion is taken place. Condensation of SiO in the transporting duct causes accumulation of solid-state SiO in the duct and results in blocking of the duct. Furthermore, the nozzle for discharging SiO vapor into the adiabatic expansion chamber tends to subject corrosion by SiO vapor and tends to be blocked by solid-state SiO condensed and accumulated in the nozzle.

Therefore, the process and system proposed in the aforementioned Japanese Patent Publication is considered as that for laboratory use and is, indeed, not applicable for industries.

In such atmosphere, although SiO has been known as one of important materials in ceramics industries, there has been no way for manufacturing large amount of fine-grained SiO powder.

#### SUMMARY OF THE INVENTION

Therefore, it is the principle object of the present invention is to provide a method and system for producing fine-grained SiO powder, which is applicable for manufacture and adapted to effectively produce a large amount of SiO powder.

Another object of the invention is to provide a mass-production process and system for fine-grained SiO powder, which can perform SiO producing process continuously.

A further object of the invention is to provide a method and system for producing SiO powder, which does not include a step of adiabatic expansion in condensing vapor-state SiO into solid-state SiO.

In order to accomplish the aforementioned and

other objects, a method for manufacturing fine-grained SiO powder includes a step of heating a reagent mixture of SiO<sub>2</sub> containing material and metallic silicon and/or carbon containing material for generating SiO vapor, and  
5 a step for condensing the generated SiO vapor in gaseous-state under the presence of non-oxidizing gas and under substantially low pressure.

Preferably, flow of the non-oxidizing gas is generated by maintaining the pressure at the position  
10 where thermal reaction to generate SiO vapor occurs at substantially low pressure. Such gas flow serves as carrier medium for transferring vapor-state SiO and/or fine-grained SiO powder to a SiO collection chamber. This successfully prevent the SiO from being condensed  
15 and accumulated in a transfer pipe or duct and thus preventing the pipe or duct from being blocked. Furthermore, substantially low pressure atmosphere encourages SiO vapor generation from the reagent mixture and requires lower heating temperature to cause SiO  
20 vapor generation.

In the preferred process, the heat-treatment for the material reagent mixture is performed in a temperature range of 1300°C to 2000°C under the pressure lower than or equal to 0.1 atm.

In the further preferred process, as the SiO<sub>2</sub> containing material, zircon, mullite, wollastonite and so forth is used. In such case, a by-product, such as zirconia, alumina, calcia and so forth of substantially high purity can be simultaneously produced. As the  
25 carbon containing material, petroleum coke, coal pitch, carbon-black, organic resin and so forth is used. Furthermore, as the non-oxidizing gas, N<sub>2</sub> gas, Ar gas, CO gas and so forth is used.  
30

In order to accomplish the aforementioned  
35 object, a SiO producing system, according to the invention, comprises a furnace defining a chamber in

which a material reagent mixture is heated at a predetermined temperature for generating SiO vapor. The heat-treatment is performed under non-oxidizing atmosphere and under substantially low pressure. The substantial low pressure is achieved into the reaction chamber through an associated SiO collection chamber. the Achievement of substantially low pressure through the SiO collection chamber causes flow of non-oxidizing gas from the reaction chamber to the SiO collecting chamber. This non-oxidizing gas flow is used as carrier medium for the SiO vapor generated in the reaction chamber or the fine-grained SiO condensed from the SiO vapor.

In the preferred construction, a non-oxidizing gas source is connected to the reaction chamber for continuously supplying the non-oxidizing gas so as to maintain the atmosphere of the reaction chamber in substantially non-oxidizing atmosphere.

Further preferably, the SiO producing system includes supply of material reagent mixture in a manner that allows continuous operation of the system for mass-production of the fine-grained SiO powder.

In addition, the system is provided with means for collecting material from which the SiO is removed. Such remained material (for example, zirconia, calcia, alumina) constitute a by-product of substantially high purity.

According to one aspect of the invention, a method for producing a fine-grained SiO powder comprises the steps of:

providing a material mixture as a mixture of a  $\text{SiO}_2$  containing material and a metallic Si and/or C containing material;

heating the material mixture under non-oxidizing and substantially low pressure atmosphere for generating vapor-state SiO;

condensing the vapor-state SiO into fine-grained solid-state SiO in gasenous state; and

collecting the condensed fine-grained solid-state SiO.

Preferably, a chamber for heating the material mixture and a chamber for condensing the vapor-state SiO are provided and a flow of non-oxidizing gas from the reaction chamber to the condensing chamber is generated for transferring the vapor-state SiO from the reaction chamber to the condensing chamber. The generation of non-oxidizing gas flow includes introduction of vacuum pressure to the reaction chamber through the condensing chamber. Further preferably, the non-oxidizing gas is continuously supplied to the reaction chamber in order to maintain the aforementioned reaction chamber in non-oxidizing atmosphere.

In order to perform the aftermentioned method, the  $\text{SiO}_2$  containing material is selected from zircon ( $\text{ZrO}_2$ ), mullite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), wollastonite ( $\text{CaO} \cdot \text{SiO}_2$ ) and  $\text{SiO}_2$  powder of high purity. The C containing material is selected from petroleum coke, coal pitch, carbon-black and organic resin. In addition, the non-oxidizing gas is selected from  $\text{N}_2$  gas, Ar gas and CO gas.

The method may further include a step of collecting remaining material mixture as by-product after removing the SiO. The by-product to be obtained is zirconia ( $\text{ZrO}_2$ ) of high purity when the  $\text{SiO}_2$  containing material is zircon. On the other hand, when the  $\text{SiO}_2$  containing material is mullite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), the by-product obtainable from the aforementioned process is alumina ( $\text{Al}_2\text{O}_3$ ) of high purity. Further, when the  $\text{SiO}_2$  containing material is wollastonite ( $\text{CaO} \cdot \text{SiO}_2$ ), the by-product to be obtained is calcia ( $\text{CaO}$ ) of high purity.

In order to implement the aforementioned

method, a device in another aspect of the invention comprises means for heating a material mixture as a mixture of a  $\text{SiO}_2$  containing material and a metallic Si and/or C containing material, under non-oxidizing and substantially low pressure atmosphere for generating vapor-state  $\text{SiO}$ , and means for condensing the vapor-state  $\text{SiO}$  into fine-grained solid-state  $\text{SiO}$  in gaseous state and collecting the condensed fine-grained solid-state  $\text{SiO}$ .

According to a further aspect of the invention, the aforementioned method is applied to the industrial process for manufacturing fine-grained  $\text{SiO}$  powder, which process comprises the steps of:

preparing a material mixture by mixing a  $\text{SiO}_2$  containing material and a metallic Si and/or C containing material;

continuously supplying the material mixture into a reaction chamber;

heating the material mixture in the reaction chamber under the presence of non-oxidizing gas and substantially low pressure atmosphere, for generating vapor-state  $\text{SiO}$ ;

transferring generated vapor-state  $\text{SiO}$  to a collecting chamber; and

cooling the vapor state  $\text{SiO}$  for causing condensation under the presence of the non-oxidizing gas and collecting condensed fine-grain  $\text{SiO}$ .

Supply of the material mixture is performed intermittently at a predetermined timing which is determined for allowing continuous operation of the  $\text{SiO}$  manufacturing process. In the alternative, supply of the material is performed continuously to cause travel of the material mixture through the reaction chamber within a predetermined period of time.

In order to implement aforementioned industrially applied  $\text{SiO}$  manufacturing process, a system

according to a still further aspect of the invention comprises first means for continuously supplying a material mixture prepared by mixing a  $\text{SiO}_2$  containing material and a metallic Si and/or C containing material, second means for receiving the material mixture from the first means and heating the material mixture under the presence of non-oxidizing gas and substantially low pressure atmosphere, for generating vapor-state  $\text{SiO}$ , third means for cooling the vapor state  $\text{SiO}$  for causing condensation under the presence of the non-oxidizing gas and collecting condensed fine-grain  $\text{SiO}$  powder, and fourth means for transferring generated vapor-state  $\text{SiO}$  from the second means to third means.

The system further comprises fifth means for introducing vacuum pressure in to the third means for generating non-oxidizing gas flow from the second means to the third means for transferring the vapor-state  $\text{SiO}$  by the gas flow. In order to maintain the atmosphere in the second means in non-oxidizing condition, the system further comprises sixth means for continuously supplying the non-oxidizing gas into the second means.

Preferably, the system further comprises seventh means for pre-heating the material mixture before supplying the material mixture into the second means so that heating of the material mixture can be effectively performed in the second means.

As set forth, according to the present invention, industrially useful by-product simultaneously of production of the fine  $\text{SiO}$  powder. Therefore, the system further comprises eighth means for cooling the material mixture after removing the  $\text{SiO}$  and collecting the remaining material as a by-product.

The first means comprises a plurality of carriages adapted to travel through the second means with the material mixture. The carriages are adapted to stop within the second means for a predetermined period



of time.

Preferably, the carriage mounts thereon a muffle which defines a reaction chamber to receive therein the material mixture and causing thermal reaction to generate the vapor-state silicon oxide therein.

The seventh means is provided upstream of the second means and the eighth means is provided downstream of the second means, and the seventh means, second means and the eighth means are aligned to form a path for the carriages.

In order to facilitate continuous operation, the system is arranged to place one of the carriage within the seventh means while the leading carriage stops within the second means and to place another carriages within the eighth means while the following carriage stops within the second means.

Alternatively, the seventh means, second means and the eighth means defines a continuous path for the material mixture, which path is filled with the material mixture and communicated with the first means for receiving continuous supply of the material mixture for causing travel of the material mixture within the path through the seventh, second and eighth means. Preferably, the seventh, second and eighth means are aligned vertically.

In the latter case, the first means comprises a hopper communicated with the top of the seventh means.

#### BRIEF DESCRIPTION OF THE DRAWINGS

The present invention will be understood more fully from the detailed description given herebelow and from the accompanying drawings of the preferred embodiments of the invention, which, however, should not be taken to limit the invention to the specific embodiment or embodiments, but are for explanation and understanding only.

In the drawings:

Fig. 1 is a fragmentary illustration showing one of fundamental structure of a SiO producing system according to the invention;

5 Fig. 2 is a fragmentary illustration of another fundamental construction of a SiO producing system according to the invention;

Fig. 3 is an electromicroscopic photograph showing yield SiO;

10 Fig. 4 is a plan view of the preferred embodiment of a SiO manufacturing system according to the invention;

Fig. 5 is a transverse section of the SiO producing system of Fig. 4, in the portion of the heating furnace;

15 Fig. 6 is a chart showing temperature distribution in the SiO producing system of Figs. 4 and 5;

20 Fig. 7 is a plan view of another preferred embodiment of a SiO manufacturing system according to the invention;

Fig. 8 is a transverse section of the SiO producing system of Fig. 7, in the portion of the heating furnace;

25 Fig. 9 is a cross-section of a further preferred embodiment of a SiO producing system according to the invention.

#### DESCRIPTION OF THE PREFERRED EMBODIMENT

30 SiO producing systems according to the present invention are generally illustrated in Figs. 1 and 2. In the arrangement of Fig. 1, the SiO producing system comprises a furnace 10 for heat-treating a reagent mixture, a SiO collection device 30 for collecting fine SiO produced by the heat-treatment in the furnace, and a vacuum source 40 for applying vacuum pressure to the  
35 furnace and the collection device.

The furnace 10 generally comprises a vacuum furnace for heat-treatment of the reagent mixture under low-pressure conditions. The furnace 10 defines a furnace chamber 12. A reagent mixture container 14 is disposed within the furnace chamber 12. The reagent mixture container 14 may comprise a crucible or the like and is of opened-top box or cylindrical configuration. The reagent mixture container 14 defines an internal reaction chamber 16. The bottom 18 of the reagent mixture container 14 has an opening 20 in communication with a non-oxidizing gas induction tube 22 in order to introduce a non-oxidizing gas into the reaction chamber 16 of the reagent mixture container 14. A heater 24, such as a high-frequency coil or resistance-heating heater or so forth, is installed in the furnace chamber 12 so as to surround the reagent mixture container 14.

The SiO collection device 30 defines a SiO collection chamber 32 therein. The SiO collection chamber 32 is connected to the vacuum pressure source 40 through a vacuum passage 42. Therefore, the SiO collection chamber 32 is maintained at a pressure substantially lower than atmospheric pressure. On the other hand, the SiO collection chamber 32 is connected to the furnace chamber 12 of the furnace 10 via a SiO collection duct 34. The SiO collection duct 34 has one end inserted into the furnace chamber 12. A horn-shaped collection hood 36 is installed on one end of SiO collection duct 34. The collection duct 34 is placed above the top opening of the reaction chamber 16 of the reagent mixture container 14. Through the SiO collection duct 34, the vacuum pressure in the collection chamber 32 of the collection device 30 is introduced into the furnace chamber 12 to hold the internal pressure in the furnace chamber substantially lower than atmospheric pressure.

The vacuum passage 42 is defined by a duct 44

which has one end 46 inserted into the SiO collection chamber 32. The end 46 of the duct 44 is covered by a SiO collection filter 48. The filter 48 serves to collect fine SiO particles drawn into the collection chamber through the collection duct 34. The collected fine SiO particles are removed through a valve 38 in the floor of the collection chamber 32.

In the preferred construction, heat-insulating layers are attached to the furnace walls of the furnace 10. Alternatively, it would be possible to provide cooling water passages within the furnace walls for cooling.

Fig. 2 shows another construction of the SiO producing system according to the invention. In this construction, a furnace 50 defines a furnace chamber 52. A muffle 54 is disposed within the furnace chamber 52 to define therein a reaction chamber 56. A reagent mixture container 58 is disposed within the reaction chamber 56. The muffle 54 is surrounded by a heater 60 so as to be heated and induce the reagent mixture to react. One or more non-oxidizing gas introducing tubes 62 introduce non-oxidizing gas into the reaction chamber 56 to expedite condensation of the SiO vapor generated by the reaction.

Similarly to the system of Fig. 1, a SiO collection device 70 collects fine SiO particles produced within the reaction chamber 56. The SiO collection device 70 defines a collection chamber 72 which is connected to the reaction chamber 56 in the furnace by means of a SiO collection duct 74. The collection chamber 72 is maintained at a pressure lower than atmospheric pressure by means of a vacuum pump 80 connected thereto through a vacuum duct 82. Since the reaction chamber 56 communicates with the collection chamber via the collection duct 74, it is also held at a pressure lower than atmospheric pressure.

A SiO collection filter 84 is attached to the end of the vacuum duct 82 inserted into the collection chamber. The collection filter 84 serves to collect the fine SiO particles introduced into the collection chamber 72 via the collection duct 74.

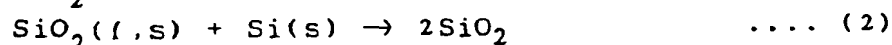
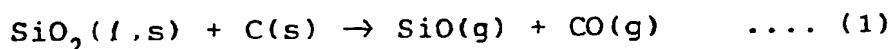
In the SiO producing process according to the present invention, the reagent mixture includes a SiO<sub>2</sub>-containing material and a Si- or C-containing material. Preferably, the SiO<sub>2</sub> in the SiO<sub>2</sub>-containing material is of high purity so as to produce fine SiO particles with high purity. High-purity SiO<sub>2</sub> can be prepared from high-purity natural quartz, water glass and so forth by reaction with acid or CO<sub>2</sub> gas. As an alternative, SiO<sub>2</sub>-containing oxide powers, such as zirconia (ZrO<sub>2</sub> . SiO<sub>2</sub>) powder, mullite (3Al<sub>2</sub>O<sub>3</sub> . 2SiO<sub>2</sub>) powder, wollastonite (CaO . SiO<sub>2</sub>) powder and so forth, can be used as the SiO<sub>2</sub>-containing material. In view of industrial application, SiO<sub>2</sub>-containing oxide powers are preferred since by-products of high purity, such as zirconia (ZrO<sub>2</sub>), alumina (Al<sub>2</sub>O<sub>3</sub>), calcia (CaO) and so forth can be produced during production of SiO.

In addition, metallic silicon powder or a carboniferous material, such as petroleum, coke, coal pitch, carbon-black organic resins and so forth are mixed with the aforementioned SiO<sub>2</sub>-containing material. If desired, a mixture of metallic silicon power and a carboniferous material can be mixed with the SiO<sub>2</sub>-containing material.

In the process according to the present invention, non-oxidizing gas is used to form a non-oxidizing atmosphere for heat-treatment of the reagent mixture. This non-oxidizing gas induces condensation of the SiO vapor generated during the heat-treatment into fine grains. Gaseous N<sub>2</sub>, Ar, CO and so forth may be used as the non-oxidizing gas.

In both of the systems of Figs. 1 and 2,

heat-treatment of the reagent mixture (the mixture of  $\text{SiO}_2$ -containing material and the Si- and/or C-containing reagent) is performed in a non-oxidizing atmosphere under a pressure below 0.1 bar. Heating temperature is in the temperature range of  $1300^\circ\text{C}$  to  $2000^\circ\text{C}$ . During heat-treatment under the conditions set forth above, reactions expressed by the following formulas occur:



At atmospheric pressure, the temperature needed to induce the reaction of formula (1) is greater than or equal to  $1750^\circ\text{C}$ . By lowering the pressure to no more than 0.1 bar, the required temperature drops to about  $1640^\circ\text{C}$  and by further lowering the pressure to below 0.01 bar, the required temperature drops further to about  $1540^\circ\text{C}$ . As will be appreciated herefrom, at low pressures, the temperature necessary for reaction is decreased.

The temperature range of  $1300^\circ\text{C}$  to  $2000^\circ\text{C}$  is preferred for effective SiO production and, at the same time, for producing the desired by-product. If the temperature is lower than  $1300^\circ\text{C}$ , SiO vapor cannot be generated. On the other hand, if the temperature is higher than  $2000^\circ\text{C}$ , sintering occurs in the mixture, which interferes with generation of SiO vapor. Furthermore, unnecessarily high heat is obviously wasteful in view of SiO production costs.

The non-oxidizing gas entering the reaction chamber displaces the SiO vapor from the surface of the mixture and effectively and quickly cools the SiO vapor to induce condensation into fine grains. Furthermore, the flow of the non-oxidizing gas from the reaction chamber to the collection chamber driven by the vacuum pressure effectively transports the condensed

fine-grained SiO into the collection chamber.

The preferred molar rate or ratios of the Si- and/or C-containing material relative to the SiO<sub>2</sub>-containing material is 0.4 to 2.0. Furthermore, the preferred volumetric rate or ratios of the non-oxidizing gas introduced into the reaction chamber in relation to the generated SiO vapor is in the range of 0.5 to 500.

Fig. 3 is a electroscopic photograph of the fine-grained SiO produced during production process according to the invention. The grain size of the SiO particles was less than or equal to 1  $\mu$ m (1000A). Under better conditions, it would be possible to obtain SiO of a uniform grain size of 100A to 200A. The color of the SiO obtained was mud yellow. The obtained SiO was amorphous. When this fine SiO is treated under atmosphere, it changes into white SiO<sub>2</sub>.

#### EXAMPLE 1

In order to prove the efficiency of the SiO producing process according to the invention, experiments were performed with the SiO producing system of Fig. 1. Experiments were performed with SiO<sub>2</sub> powder containing 99.5% SiO<sub>2</sub>, zircon powder containing 99.5% ZrO<sub>2</sub> and SiO<sub>2</sub>, and wollastonite powder containing 99.5% CaO and SiO<sub>2</sub>. The rate or ratios of Si- and/or C-containing material, heating conditions and results are shown in the following table I. The yield of SiO is given in relation to theoretical yield in weight percent (wt%).

SiO producing process according to the conventional art was also use so as to obtain results for comparison. The SiO yields were compared to prove the efficiency of the inventive process.

	REAGENT MIXTURE			HEAT-TREATMENT CONDITION					SIO COLLECTION RATE (wt%)
	SIO <sub>2</sub> SOURCE	REDUCTION AGENT	MIXTURE RATE	TEMP. (°C)	TIME (hr)	PRESSURE (atm)	SPECIES	GAS VOLUME RATIO	
COMP. EX. 1	SiO <sub>2</sub>	COAL PITCH	C/ SiO <sub>2</sub> =1.3	1550°C	5	0.0002	-	0	15
COMP. EX. 2	"	"	" =1.3	1550°C	5	0.2	Ar	5	45
EX. 1	"	"	" =1.3	1550°C	5	0.09	Ar	5	67
COMP. EX. 3	"	"	" =1.3	1250°C	100	0.001	Ar	1	25
EX. 2	"	"	" =1.3	1400°C	100	0.001	Ar	1	57
COMP. EX. 4	"	"	" =0.3	1600°C	3	0.01	Ar	5	45
EX. 3	"	"	" =0.5	1600°C	3	0.01	Ar	5	60
EX. 4	"	"	" =2.0	1600°C	3	0.01	Ar	5	81
COMP. EX. 5	"	"	" =2.5	1600°C	3	0.01	Ar	5	43
EX. 5	"	Si	Si/ SiO <sub>2</sub> =1.2	1700°C	2	0.01	H2	10	170
EX. 6 (ZrO <sub>2</sub> . SiO <sub>2</sub> )		PETROLEUM COKE	C/ SiO <sub>2</sub> =1.0	1600°C	3	0.01	H2	10	93
EX. 7	"	Si	Si/ SiO <sub>2</sub> =1.0	1700°C	2	0.01	H2	10	180
COMP. EX. 6 (CaO . SiO <sub>2</sub> )		CARBON BLACK	C/ SiO <sub>2</sub> =1.5	1550°C	10	0.01	Ar	0.3	31
EX. 8	"	"	" =1.5	1550°C	10	0.01	Ar	0.6	59
EX. 9	"	"	" =1.5	1550°C	10	0.1	Ar	50	85

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As will be appreciated from the TABLE I above, the yield of fine-grained SiO is remarkably improved by the inventive process.

EXAMPLE 2

5 Another experiments were performed using zircon powder containing 99.5%  $ZrO_2$  and  $SiO_2$ . Average grain size of the zircon powder was 0.95  $\mu m$ . The zircon powder was mixed with carbon-black which is available in the market under the tradename "SHI-SUTOU 6" from  
10 Tokai Carbon K.K. The grain size of the carbon black was 210A. A uniform mixture of zircon power and the carbon-black was prepared. The mixture was shaped into a solid cylindrical mass 15 mm in diameter x 300 mm high. A plurality of cylindrical masses were prepared.  
15 The SiO producing process according to the present invention was performed utilizing the SiO producing system of Fig. 2 under the conditions shown in the following TABLE II. In these experiments, the purity of the zirconia powder produced as a by-product and the  
20 yield of SiO were checked.

The mol ratio ( $C/SiO_2$ ) of  $SiO_2$  in the zircon powder and C in the carbon-black was adjusted to be 1.2. The yield of SiO is given in relation to theoretical yield in percent by weight (wt%). Ar gas was used as a  
25 non-oxidizing gas in volumetric rate or ratios of 10:1 relative to the SiO vapor.

30

35

TABLE II

	HEAT-TREATMENT CONDITION					ZIRCONIA PURITY (wt%)	SiO COLLECTION RATE (wt%)
	ZIRCON + C WEIGHT (kg)	TEMP (°C)	TIME (hr)	PRESSURE (atm)	atmosphere		
EX. 10	3	1500	5	0.01	Ar	98.6	90
EX. 11	3	1600	3	0.01	Ar	98.7	95
EX. 12	10	1500	6	0.01	Ar	98.5	95
EX. 13	10	1600	4	0.01	Ar	98.7	96

As will be appreciated from the foregoing experiments, the SiO producing process according to the present invention provides a higher SiO yield than the prior art. Therefore, by utilizing the inventive process in industry, the efficiency of fine-grained SiO production can be increased. Furthermore, in parallel to the production of fine-grained SiO, high purity by-products, such as zirconia, alumina, calcia and so forth can be obtained.

The following disclosure is directed to the preferred embodiments of the SiO manufacturing processes and systems for industrial implementation of the aforementioned process of SiO production according to the present invention.

Continuous operation of the producing plant or system is regarded as an essential factor in view of production capacity and efficiency. Therefore, the following embodiments are directed to continuous SiO production.

Figs. 4 and 5 show another embodiment of a SiO manufacturing system according to the present invention. The first embodiment of the SiO manufacturing system generally comprises a heating furnace 100, a pre-heating chamber 102, a cooling chamber 104, and SiO collection chambers 106. The pre-heating chamber 102, the heating furnace 100 and the cooling chamber 104 are arranged in-line along a platform 108. A furnace chamber 110 in the heating furnace 100 is connected to the pre-heating chamber 102 and the cooling chamber 104. Doors 112 and 114 separate the pre-heating chamber 102 from the furnace chamber 110 and the furnace chamber from the cooling chambers 104. The other end of the pre-heating chamber 102 is provided with a door 116. Similarly, the other end of the cooling chamber 104 is closed by a door 118.

A pair of rails 122 are fixedly secured to the

floor 120 of the platform 108, thus defining a railway extending through the pre-heating chamber 102, the furnace chamber 110 and the cooling chamber 104. One or more carriages 124 run along the railway carrying a reagent mixture 126. As set forth above, the reagent mixture 126 is composed of a  $\text{SiO}_2$ -containing material, such as high-purity  $\text{SiO}_2$  powder, zircon powder, mullite powder, wollastonite powder and so forth, and a Si- and/or C-containing material, such as metallic silicon, petroleum, coke, coal pitch, carbon-black, organic resin and so forth. This reagent mixture is received within a material container 128. A plurality of the material containers 128 are mounted on the carriage 124 to be carried along the railway 122.

In order to facilitate continuous operation of the SiO producing system, it would be preferable to provide more than three carriages 124, each transporting a plurality of reagent mixture containers 128. The carriages 124 may driven step-wise so as to stop at the pre-heating chamber 102, the furnace chamber 110 and the cooling chamber 104 for a predetermined period of time. The period of time the carriages 124 spend in each chamber would be determined according to the heat-treatment time needed to produce fine-grained SiO in the furnace chamber 110.

The pre-heating chamber 102 is defined by vertically extending side walls 130 and a ceiling (not shown). The pre-heating chamber 102 has an entrance opening 134 and an exit opening 136 respectively closed by doors 116 and 112. The side walls 130, the ceiling and the doors 112 and 116 are provided with heat-insulating liners. Alternatively, the side walls 130, the ceiling and the doors 112 and 116 can be made of a substance containing a heat-insulating component. Furthermore, if necessary, the side walls 130 and the ceiling may be provided with cooling water passages

extending therethrough for effective cooling.

5 A heater means 130 is disposed within the pre-heating chamber 102. As will be seen from Fig. 4, the heater means 130 comprises heat generators, such as a high-frequency coil, resistance heater or the like, arranged on either side of the path of the carriages 124. One or more non-oxidizing gas inlets 140 in the side wall 130 and/or the ceiling admit non-oxidizing gas in the pre-heating chamber 102. The non-oxidizing gas inlets 140 are connected to induction pipes 142 connected in turn to a non-oxidizing gas source (not shown). An exhaust port 144 in the side wall 130 or the ceiling is connected to an exhaust pipe 146 to vent the inert gas atmosphere.

15 The doors 112 and 116 allow the carriage 124 with the reagent mixture containers 128 to pass when open and insulate the pre-heating chamber 102 from the atmosphere and from the furnace chamber during pre-heating when closed. As shown in Fig. 6, pre-heating is performed at a temperature approximately 1000 °C.

25 It would be convenient to provide actuators for the doors 112 and 116 for automatically opening and closing the doors. More preferably, the system may include a door control system including sensors for detecting when carriages 124 are approaching the entrance opening 134 and the exit opening 136 and automatically activating the actuators to open and close the doors. In this case, the progress of the carriages 124 along the railway 122 will be controlled.

30 Side walls 148 and a ceiling 150 of the heating furnace 100 define the furnace chamber 110. Similarly to the pre-heating chamber 102, the furnace chamber 110 has an entrance opening 152 and an exit opening 154. The entrance opening 152 adjoins the exit opening 136 of the pre-heating chamber 102.

Communication between the pre-heating chamber 102 and the furnace chamber 110 is established and blocked depending upon the position of the door 112. Likewise, the exit opening 154 of the furnace chamber 110 is closed by the door 114. The side walls 148, the ceiling 150, the door 114 are provided with heat-insulating liners, or are made of a substance containing a heat-insulating component.

A muffle 156 in the furnace chamber 110 surrounds the carriage 124 when in the heating position. The muffle 156 defines a reaction chamber 158 in which the reagent mixture reacts to generate the SiO vapor.

A heating means 160 installed in the furnace chamber 110 surrounding the muffle 156 heats the reagent mixture on the carriage 124 within the reaction chamber 158 to a temperature sufficient to generate SiO vapor, i.e. in a temperature range of 1300 °C to 2000 °C as set forth with respect to Fig. 1. Similarly to the heating means in the pre-heating chamber 102, the heating means 160 of the furnace chamber 110 may be high-frequency coils, resistance heaters, or the like arranged along both sides of the carriage path.

The side walls 150 have communication passages 162 which connect the furnace chamber 110 to the SiO collection chambers 106. SiO collection ducts 164 extend from the muffle 156 and pass through the communication passages 162 to establish communication between the reaction chamber 158 and the SiO collection chamber 106. Auxiliary heaters 166 are provided within the communication passages 162 surrounding the SiO collection pipes 164. The auxiliary heaters 166 heat the SiO collection pipes to keep the SiO vapor generated in the reaction chamber 158 in vapor form.

Heat insulator plates 168 oppose the outlet of the SiO collection pipes 164. The heat insulator plates 168 extend downward from extensions 170 of the side

walls.

Each SiO collection chamber 106 is divided into two sections 172 and 174 communicating with each other through a communication passage 176 near the ceilings of the sections. A vacuum duct 178 is connected to a vacuum source, such as vacuum pump (not shown), and inserted into the section 174 of the SiO collection chamber 106 for introducing vacuum pressure. The vacuum duct 178 has a bug-filter 180 at the end inserted into the section 174 of the SiO collection chamber. The bug-filter 180 prevents SiO drawn from the reaction chamber 158 to the SiO collection chamber from flowing through the vacuum duct 178. The sections 172 and 174 of the SiO collection chamber 106 respectively have outlet valves 182 and 184 for removing the collected SiO. To facilitate removal of the collected SiO, the floors of the sections 172 and 174 of the SiO chambers are designed to act as hoppers.

The SiO yield may be taken to other sections of the factory for further treatment, packaging and so forth.

In order to preserve the non-oxidizing atmosphere in the reaction chamber 158, non-oxidizing gas has to be added during heat-treatment of the reagent mixture. Therefore, one or more non-oxidizing gas induction pipes 186 pass through the furnace walls. In the shown embodiment, the non-oxidizing gas induction pipes 186 extend into the furnace chamber 110 through the ceiling and the floor of the carriage platform. Each induction pipe extending through the ceiling of the furnace 100 passes through the muffle 156 to the reaction chamber 158. On the other hand, the induction pipes 186 extending through the floor of the carriage platform may be vertically movable so that it may pass through the carriage and discharge the non-oxidizing gas directly into the reagent mixture containers 128 on the

carriage 124. The pipe 186 extending through the floor may be lowered while the carriage 124 is moving so as not to interfere with the carriage's travel. Alternatively, the carriage 124 may have a discharge nozzle, the upper end of which is directed toward the containers thereon and the lower end of which extend down through the carriage floor. The discharge nozzle carried by the carriage is connected to the induction pipe 186 by means of an appropriate coupler or connector when the carriage 124 is properly positioned for heat-treatment.

Similarly to the foregoing pre-heating chamber 102, the cooling chamber 104 is defined by vertically extending side walls 188 and a ceiling (not shown). One or more non-oxidizing gas induction ports 192 and an exhaust port 194 for inert gas replacement and exhausting of the non-oxidizing gas pass through the side walls 188. The induction ports 192 are connected to a non-oxidizing gas source through non-oxidizing gas induction pipes 196. On the other hand, the exhaust port 194 is connected to an exhaust pipe 198.

The heat distribution in the pre-heating chamber 102, the furnace chamber 110 and the cooling chamber 104 is illustrated in Fig. 6. As shown in Fig. 6, the reagent mixture 126 on the carriage 124 is heated to about 100°C in the pre-heating chamber 102. The pre-heating chamber 102 is at atmospheric pressure, i.e. 1 atm. Non-oxidizing gas, e.g. N<sub>2</sub> gas or Ar gas, is introduced into the pre-heating chamber through the non-oxidizing gas inlet 140. Therefore, the reagent mixture 126 is pre-heated under non-oxidizing conditions at atmospheric pressure. In the pre-heating chamber 102, the temperature of the reagent mixture 126 rises at a rate of approximately 300°C per hour.

The carriage 124 carrying the reagent mixture 126 in the container 128 stays within the pre-heating



chamber throughout this pre-heating treatment. After a predetermined period of time which should be sufficiently long to pre-heat the reagent mixture to about 1000°C, the door 112 is actuated to open to allow the carriage 124 to enter the furnace chamber 110. At the same time, the door 116 opens to allow the next carriage 124 to enter the pre-heating chamber.

In the furnace chamber 110, the reagent mixture 126 on the carriage 124 is heated to about 1600°C by means of the heating means 160. The rate of increase in the reagent mixture temperature in the reaction chamber 158 is about 200°C per hour until the reagent mixture 126 is heated to 1600°C. Heat-treatment is performed under a non-oxidizing atmosphere of non-oxidizing gas, e.g. N<sub>2</sub>, Ar or the like. The pressure in the furnace chamber 110 is held to approximately 0.05 atm. By such heat treatment, SiO vapor is generated by the reagent mixture 126. SiO vapor is transported by the flow of the non-oxidizing gas to the SiO collection chambers 106 through the SiO collection ducts 164. As the SiO vapor travels to the SiO collection chambers 106, and within the SiO collection chamber 106 itself, the SiO vapor is cooled until it condenses into fine-grained, solid-state SiO.

As set forth above, since the inner end of the vacuum duct 178 for introducing vacuum pressure into the SiO collection chamber 106 and furnace chamber 110 is provided with the bug filter 180, gaseous or particulate SiO will not enter the vacuum duct. Therefore, the problem of pollution does not arise.

The consensed SiO is accumulated in the hoppers in the SiO collection chambers 106. The outlet valves 182 and 184 are then opened to retrieve the collected SiO.

After a predetermined period of time which should be sufficient to remove all of the SiO from the

reagent mixture 126, the door 114 is opened to allow the carriage 124 to move into the cooling chamber 104. At the same time, the carriage 124 in the pre-heating chamber 102 enters the furnace chamber for the next SiO producing heat-treatment. Furthermore, the next carriage 124 is moved into the pre-heating chamber 102 for preparation for the next SiO producing heat-treatment in the furnace chamber.

The reagent mixture 126 on the carriage 124 is forcibly cooled by introducing a relatively cool non-oxidizing gas into the cooling chamber 104. Therefore, within the cooling chamber, the non-oxidizing gas serves as cooling medium for the reagent mixture. The cooling chamber 104 is at atmospheric pressure, i.e. 1 atm. After being sufficiently cooled, the by-product, such as zirconia, alumina, calcia and so forth, which depends on the starting material such as zircon, mullite, wollastonite and so forth, used as an SiO<sub>2</sub>-containing material, can be retrieved. The resultant by-product will be of high purity.

Figs. 7 and 8 show the second embodiment of the SiO producing system according to the present invention. So as to avoid redundant recitation for the same structural components as that in the first embodiment, the same references numerals are used for identifying the same components and neglect detailed disclosures thereabout. This second embodiment of the SiO producing system is adapted to produce larger amount of SiO of fine grain in comparison with that produced in the first embodiment.

Therefore, the carriage 124 is adapted to larger number of the reagent mixture containers 128 with the reagent mixture. So that larger amount of the reagent mixture of the SiO containing material and Si and/or C containing material, larger volume of reaction chamber 200 is required. The reaction chamber 200 is

formed by a muffle 202. The muffle 202 is mounted on the carriage 124 to be carried with the reagent mixture 126 in the containers 128 on the carriage. The muffle 202 is formed with a plurality of through openings 204 through which SiO vapor generated during the heat-treatment flows to the SiO collection chambers 106 with the flow of non-oxidizing gas. For higher efficiency of transfer of the SiO vapor to the collection chambers 106, the through openings 204 are formed at the positions respectively corresponding to a plurality of SiO collection ducts 206 extending through the side walls 148 of the furnace 100.

The SiO collection chamber 106 is separated in to two sections 208 and 210, similarly to the foregoing embodiment. A communication passage 212 is provided between the sections 208 and 210 of the SiO collection chamber 106 so as to establish fluid communication therebetween. The communication passage 212 has an end opening to the section 208, to which a filter 214 is fitted. Similarly to the former embodiment, the heat insulating plate 168 is provided within the section 208 for insulating heat radiated from the furnace chamber 110. The aforementioned end of the communication passage 212 opens at relatively lower portion of the section 208. The other end of the communication passage 212 opens at the top of the other section 210. The section 210 has smaller volume than that of the section 208. The vacuum duct 178 with the bug-filter 180. The section 210 also has a bottom serving as a hopper with and an outlet valve 216 for removing the fine-grained solid-state SiO from the SiO collection chamber 106.

On the other hand, in order to keep the atmosphere in the furnace chamber 110 in non-oxidizing atmosphere, which furnace chamber has greater volume than that in the former embodiment for the larger capacity of SiO production, additional non-oxidizing gas

induction pipe 218 is provided. The addition non-oxidizing gas induction pipe 218 extends through the ceiling 148 of the furnace and further extends through the ceiling of muffle 202. So as not to interfere travel of the carriage 124, the pipe 218 may be vertically movable toward and away from the carriage 124. For instance, while the carriage 124 is stopped at the position in the furnace, where the heat-treatment for the reagent mixture is to be taken place, the pipe 218 is in the lowered position to discharge non-oxidizing gas into the reaction chamber 200. On the other hand, when the carriage 124 travels from the pre-heating chamber 102 to the furnace chamber 110 or from the furnace chamber to the cooling chamber 104, the pipe 218 is shifted upwardly out of the muffle 202 to allow the carriage 124 with the reagent mixture containers 128 and the muffle 202 to travel.

In the alternative, it would be possible to provide a non-oxidizing gas discharge nozzle for the muffle 202 and connect the discharge nozzle to the pipe 218 by means of an appropriate coupler or connector.

With the aforementioned construction, the SiO production system of Figs. 7 and 8 operates substantially the same manner as that recited with respect to the former embodiment of Figs. 4 and 5.

Fig. 9 shows another embodiment of the SiO producing system according to the present invention. In this embodiment, SiO production process according to the present invention is implemented by means of a vertical furnace 300, to which the aforementioned reagent mixture, i.e. mixture of  $\text{SiO}_2$  containing material and Si and/or C containing material is supplied continuously for continuous production of fine-grained SiO and by-product.

The vertical furnace 300 of this embodiment defines a vertically extending furnace chamber 302. The

furnace chamber 302 is divided into three zones, i.e. a pre-heating zone 304, a heat-treatment zone 306 and a cooling zone 308. An essentially cylindrical muffle 310 extends through overall length of the furnace chamber 302 through the pre-heating chamber 304, the heat-treatment zone 306 and the cooling zone 308. The muffle 310 further extends downwardly through the furnace 300 to form a cylindrical extension 309. The lower end of the cylindrical extension 309 is connected to a by-product collection chamber 312. The by-product collection chamber 312 has an outlet valve 313 for removing the by-product collected and accumulated therein. A gas replacement chamber 315 is defined below the by-product collecting section 312. The gas-replacement chamber 315 is communicated with an exhaust duct.

The top of the muffle 310 is connected to a hooper 312 for continuously supplying the reagent mixture, through a supply control valve 314, a gas replacement chamber 316 and a supply control valve 318. The gas replacement chamber 316 is connected to an exhaust duct 320 for exhausting waste gas. Non-oxidizing gas induction pipes 322 are connected to the top of the muffle 310 at the outside of the furnace 300 and at adjacent the lower end of the cylindrical extension 309. The muffle 310 also has a pair of blanches 324 which serve as SiO collection ducts. The SiO collection ducts 324 are communicated with SiO collection chambers 326. The SiO collection chambers 326 are defined by outer cell thereof, which outer cells are made of steel plate.

Similarly to the former embodiments, the SiO collection chambers 326 of this embodiment are respectively separated into two sections 328 and 330. Bottoms of the respective sections 328 and 330 are formed to serve as hoppers. Outlet valves 332 and 334

are provided at the bottoms of the sections 328 and 330 for removing the fine-grained SiO collected and accumulated therein.

A vacuum duct 336 is inserted into the section 330 in order to connect the section 330 with a vacuum source (not shown). By the vacuum pressure introduced into the section 330, the furnace chamber 302 and the interior of the muffle 310 are maintained at vacuum pressure.

As will be seen from Fig. 9, the muffle 310 has essentially smaller diameter than the inner diameter of the furnace 300 to define therebetween a heating chamber 338. Heaters 340, 342 and 344 are provided within the heating chamber 338 surrounding the muffle 310. The heater 340 is disposed within the pre-heating zone 304 for heating the reagent mixture in the pre-heating zone at a temperature upto approximately 1000°C. The heater 342 is disposed within the heat-treatment zone 306 is adapted to heat the reagent mixture passing the heat-treatment zone at an essentially constant temperature, i.e. 1600°C. On the other hand, the heater 344 in the cooling zone 344 generates substantially low temperature in comparison with that generated in the pre-heating zone 304 and the heat-treatment zone 306.

Burden supports 346 and 348 are provided within the by-product collection chamber 312 opposing the lower end of the cylindrical extension 309 of the muffle 310. The burden supports 346 and 348 are respectively movable perpendicularly to the axis of the furnace so as to adjust the amount of the by-product falling into the by-product collection chamber 312 and whereby adjusting speed of downward travel of the reagent mixture filled in the muffle 310. The passage area defined by the burden support 346 and 348 may be controlled in relation to the path area defined in the

supply control valves 314 and 318.

In the SiO producing process according to the invention with the SiO producing system of Fig. 9, the internal space of the muffle 310 is filled by the reagent mixture. The reagent mixture in the internal space of the muffle 310 travels through the pre-heating zone 304, the heat-treatment zone 306 and the cooling zone 308. During this process, non-oxidizing gas is introduced into the internal space of the muffle 310 so that heat-treatment for generating SiO producing process under non-oxidizing atmosphere. Pressure in the furnace chamber 302 is maintained at vacuum by the effect induction of the vacuum through the vacuum duct 336 into the SiO collection chamber 326.

Similarly to the foregoing embodiment, the reagent mixture in the muffle 310 is pre-heated in the pre-heating zone at about  $1000^{\circ}\text{C}$  along the heat distribution curve illustrated in Fig. 6, during downward travel. The reagent passing the pre-heating zone 304 subsequently enter the heat-treatment zone 306. In the region in the heat-treatment zone, where the SiO collection ducts 324 are provided, the temperature of the reagent mixture is maintained constant at about  $1600^{\circ}\text{C}$  which is high enough to cause generation of SiO vapor. The SiO vapor generated from the reagent mixture due to thermal reaction caused in the reagent mixture, is drawn into the SiO collection chamber with the non-oxidizing gas flow. Heaters 350 provided surrounding the SiO collection ducts 324 serves for maintain the SiO in vapor state. In the SiO collection chamber 326, the SiO vapor is cooled condensed into fine-grained solid-state SiO. By continuously processing the reagent mixture, fine-grained SiO can be accumulated within the SiO collection chamber 326. The collected SiO is removed from the SiO collection chamber 326 through the outlet valve 328.

On the other hand, the remaining material from which the SiO is removed are transferred to the cooling zone 306 to be cooled. The cooled SiO removed material serves as by-product of substantially high purity. Such  
5 by-product is accumulated within the by-product collecting chamber 312 and removed therefrom through the outlet valve 313.

As will be appreciated herefrom, the embodiment of Fig. 9 facilitate continuous processing for SiO production and can provide substantially high  
10 efficiency in production of fine-grained SiO.

Therefore, the present invention fulfills all of the objects and advantages sought therefor.

While the present invention has been disclosed  
15 hereabove in terms of the specific embodiments which implement the present invention, it should be appreciated that the present invention can be implemented in any ways differed from the shown embodiments. Furthermore, various modifications of the  
20 shown embodiment would be possible to reach the similar results. Therefore, the present invention should be understood to include all the embodiments and modifications which can embody the invention without departing from the principle of the invention, which is  
25 set out in the appended claims.

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WHAT IS CLAIMED IS:

1. A method for producing a fine-grained silicon monoxide powder comprising the steps of:

5 providing a material mixture as a mixture of a silicon dioxide containing material and a metal silicon and/or carbon containing material;

heating said material mixture under non-oxidizing and substantially low pressure atmosphere for generating vapor-state silicon monoxide;

10 condensing said vapor-state silicon monoxide into fine-grained solid-state silicon monoxide within gasenous atmosphere; and

collecting the condensed fine-grained solid-state silicon monoxide.

15 2. A method as set forth in claim 1, which further comprises the steps of providing a chamber for heating said material mixture, providing a chamber for condensing said vapor-state silicon monoxide, generating  
20 a flow of non-oxidizing gas from said reaction chamber to said condensing chamber for transferring said vapor-state silicon monoxide from said reaction chamber to said cendensing chamber.

25 3. A method as set forth in claim 2, wherein said non-oxidizing gas flow generating step includes introduction of vacuum pressure to said reaction chamber through said condensing chamber.

30 4. A method as set forth in claim 3, wherein said non-oxidizing gas is continuously supplied to said reaction chamber.

35 5. A method as set forth in claim 4, wherein said heating step is performed by a heating temperature in a range of 1300 °C to 2000 °C under the pressure of less

than or equal to 0.1 atm.

5 6. A method as set forth in claim 5, wherein said silicon dioxide containing material is selected among zircon ( $\text{ZrO}_2$ ), mullite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ), wollastonite ( $\text{CaO} \cdot \text{SiO}_2$ ) and silicon dioxide powder of high purity.

10 7. A method as set forth in claim 6, wherein said carbon containing material is selected among petroleum coke, coal pitch, carbon-black and organic resin.

15 8. A method as set forth in claim 7, wherein said non-oxidizing gas is selected among  $\text{N}_2$  gas, Ar gas and CO gas.

20 9. A method as set forth in claim 5, which further comprises a step of collecting remaining material mixture after removing said silicon monoxide as by-product.

10 10. A method as set forth in claim 9, wherein said silicon dioxide containing material is zircon ( $\text{ZrO}_2 \cdot \text{SiO}_2$ ).

25 11. A method as set forth in claim 10, wherein said by-product is zirconia ( $\text{ZrO}_2$ ) of high purity.

30 12. A method as set forth in claim 9, wherein said silicon dioxide containing material is mullite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ).

13. A method as set forth in claim 12, wherein said by-product is alumina ( $\text{Al}_2\text{O}_3$ ) of high purity.

35 14. A method as set forth in claim 9, wherein said silicon dioxide containing material is wollastonite

(CaO.SiO<sub>2</sub>).

15. A method as set forth in claim 14, wherein said by-product is calcia (CaO) of high purity.

5 16. A device for producing a fine-grained silicon monoxide powder comprising:

10 means for heating a material mixture as a mixture of a silicon dioxide containing material and a metal silicon and/or carbon containing material, under non-oxidizing and substantially low pressure atmosphere for generating vapor-state silicon monoxide; and

15 means for condensing said vapor-state silicon monoxide into fine-grained solid-state silicon monoxide within gaseous atmosphere and collecting the condensed fine-grained solid-state silicon monoxide.

17. A device as set forth in claim 16, wherein said heating means comprises a reaction chamber for heating said material mixture, and said condensing means includes a condensing chamber for condensing said vapor-state silicon monoxide, and said reaction chamber and said condensing chamber are communicated with each other for generating a flow of non-oxidizing gas from said reaction chamber to said condensing chamber for transferring said vapor-state silicon monoxide from said reaction chamber to said condensing chamber.

18. A device as set forth in claim 17, which further comprises means for generating said non-oxidizing gas flow, which non-oxidizing gas flow generating means includes means for introducing vacuum pressure to said reaction chamber through said condensing chamber.

19. A device as set forth in claim 18, wherein

said non-oxidizing gas is continuously supplied to said reaction chamber.

5           20.           A device as set forth in claim 19, wherein said heating means performs heating of said reagent mixture by a heating temperature in a range of 1300°C to 2000 °C under the pressure of less than or equal to 0.1 atm.

10           21.           A device as set forth in claim 20, wherein said silicon dioxide containing material is selected among zircon ( $ZrO_2$ ), mullite ( $Al_2O_3 \cdot 2SiO_2$ ), wollastonite ( $CaO \cdot SiO_2$ ) and silicon dioxide powder of high purity.

15           22.           A device as set forth in claim 21, wherein said carbon containing material is selected among petroleum coke, coal pitch, carbon-brack and organic resin.

20           23.           A device as set forth in claim 22, wherein said non-oxidizing gas is selected among  $N_2$  gas, Ar gas and CO gas.

25           24.           A device as set forth in claim 19, which further means for collecting remaining material removed said silicon monoxide as by-product.

30           25.           A device as set forth in claim 24, wherein said silicon dioxide containing material is zircon ( $ZrO_2 \cdot SiO_2$ ).

          26.           A device as set forth in claim 25, wherein said by-product is zirconia ( $ZrO_2$ ) of high purity.

35           27.           A device as set forth in claim 24, wherein said silicon dioxide containing material is mullite

( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ).

28. A device as set forth in claim 27, wherein said by-product is alumina ( $\text{Al}_2\text{O}_3$ ) of high purity.

29. A device as set forth in claim 24, wherein said silicon dioxide containing material is wollastonite ( $\text{CaO} \cdot \text{SiO}_2$ ).

30. A device as set forth in claim 29, wherein said by-product is calcia ( $\text{CaO}$ ) of high purity.

31. A process for manufacturing fine-grained silicon monoxide powder comprising the steps of:

preparing a material mixture by mixing a silicon dioxide containing material and a metallic silicon and/or carbon containing material;

continuously supplying said material mixture into a reaction chamber;

heating said material mixture with in reaction chamber under the presence of non-oxidizing gas and substantially low pressure atmosphere, for generating vapor-state silicon monoxide;

transferring generated vapor-state silicon monoxide to a collecting chamber ; and

cooling said vapor state silicon monoxide for causing condensation under the presence of said non-oxidizing gas and collecting condensed fine-grain silicon powder.

32. A process as set forth in claim 31, which further comprises a step of introducing vacuum pressure in to said collecting chamber for generating non-oxidizing gas flow from said reaction chamber to said collecting chamber for transferring said vapor-state silicon monoxide by the gas flow.

33. A process as set forth in claim 32, which further comprises a step of continuously supplying said non-oxidizing gas into said reaction chamber.

5

34. A process as set forth in claim 33, which further comprises a step of pre-heating said material mixture before supplying the material mixture into said reaction chamber.

10

35. A process as set forth in claim 34, which further comprises a step of cooling said material mixture after removing said silicon monoxide and collecting the remaining material as a by-product.

15

36. A process as set forth in claim 35, wherein said heating step is performed by a heating temperature in a range of 1300°C to 2000°C under the pressure of less than or equal to 0.1 atm.

20

37. A process as set forth in claim 35, wherein said supply of said material mixture is performed intermittently at a predetermined timing which is determined for allowing continuous operation of the silicon monoxide manufacturing process.

25

38. A process as set forth in claim 35, wherein said supply of said material is performed continuously to cause travel of said material mixture through said reaction chamber within a predetermined period of time.

30

39. A process as set forth in claim 36, wherein said silicon dioxide containing material is zircon ( $\text{ZrO}_2 \cdot \text{SiO}_2$ ).

35

40. A process as set forth in claim 39, wherein

said by-product is zirconia ( $ZrO_2$ ) of high purity.

41. A process as set forth in claim 36, wherein said silicon dioxide containing material is mullite ( $Al_2O_3 \cdot 2SiO_2$ ).

42. A process as set forth in claim 41, wherein said by-product is alumina ( $Al_2O_3$ ) of high purity.

43. A process as set forth in claim 36, wherein said silicon dioxide containing material is wollastonite ( $CaO \cdot SiO_2$ ).

44. A process as set forth in claim 43, wherein said by-product is calcia ( $CaO$ ) of high purity.

45. A system for manufacturing fine-grained silicon monoxide powder comprising:

first means for continuously supplying a material mixture prepared by mixing a silicon dioxide containing material and a metallic silicon and/or carbon containing material;

second means for receiving said material mixture from said first means and heating said material mixture under the presence of non-oxidizing gas and substantially low pressure atmosphere, for generating vapor-state silicon monoxide;

third means for cooling said vapor state silicon monoxide for causing condensation under the presence of said non-oxidizing gas and collecting condensed fine-grain silicon powder; and

fourth means for transferring generated vapor-state silicon monoxide from said second means to third means.

46. A system as set forth in claim 45, which

further comprises fifth means for introducing vacuum pressure in to said third means for generating non-oxidizing gas flow from said second means to said third means for transferring said vapor-state silicon monoxide by the gas flow.

47. A system as set forth in claim 46, which further comprises sixth means for continuously supplying said non-oxidizing gas into said second means.

48. A system as set forth in claim 47, which further comprises seventh means for pre-heating said material mixture before supplying the material mixture into said second means.

49. A system as set forth in claim 48, which further comprises eighth means for cooling said material mixture after removing said silicon monoxide and collecting the remaining material as a by-product.

50. A system as set forth in claim 49, wherein said second means is performed by a heating temperature in a range of 1300 °C to 2000 °C under the pressure of less than or equal to 0.1 atm.

51. A system as set forth in claim 50, wherein said silicon dioxide containing material is zircon ( $\text{ZrO}_2 \cdot \text{SiO}_2$ ).

52. A method as set forth in claim 51, wherein said by-product is zirconia ( $\text{ZrO}_2$ ) of high purity.

53. A system as set forth in claim 50, wherein said silicon dioxide containing material is mullite ( $\text{Al}_2\text{O}_3 \cdot 2\text{SiO}_2$ ).



54. A system as set forth in claim 53, wherein said by-product is alumina ( $Al_2O_3$ ) of high purity.

5 55. A system as set forth in claim 50, wherein said silicon dioxide containing material is wollastonite ( $CaO.SiO_2$ ).

56. A system as set forth in claim 55, wherein said by-product is calcia ( $CaO$ ) of high purity.

10 57. A system as set forth in 45, wherein said first means comprises a plurality of carriages adapted to travel through said second means with said material mixture.

15 58. A system as set forth in claim 58, wherein said carriages are adapted to stop within said second means for a predetermined period of time.

20 59. A system as set forth in claim 58, wherein said carriage mounts thereon a muffle which defines a reaction chamber to receive therein said material mixture and causing thermal reaction to generate said vapor-state silicon monoxide therein.

25 60. A system as set forth in claim 59, which further comprises seventh means for pre-heating said material mixture before supplying the material mixture into said second means and eighth means for cooling said material mixture after removing said silicon monoxide and collecting the remaining material as a by-product.

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35 61. A system as set forth in claim 60, wherein said seventh means is provided upstream of said second means and said eighth means is provided downstream of said second means, and said seventh means, second means

and said eighth means are aligned to form a path for said carriages.

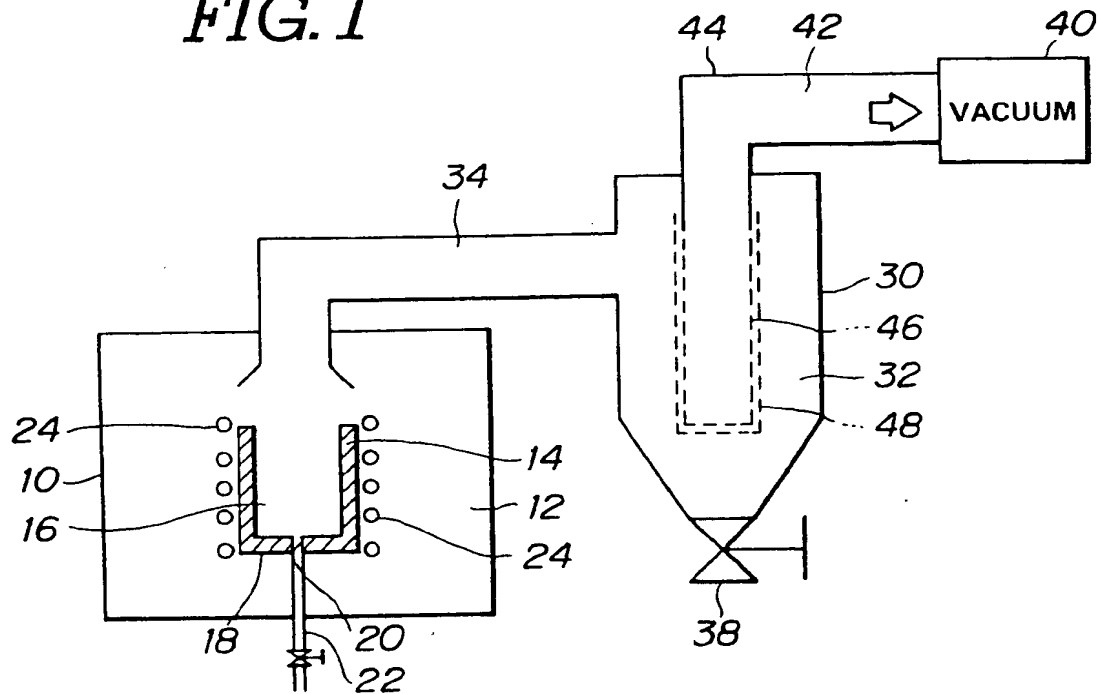
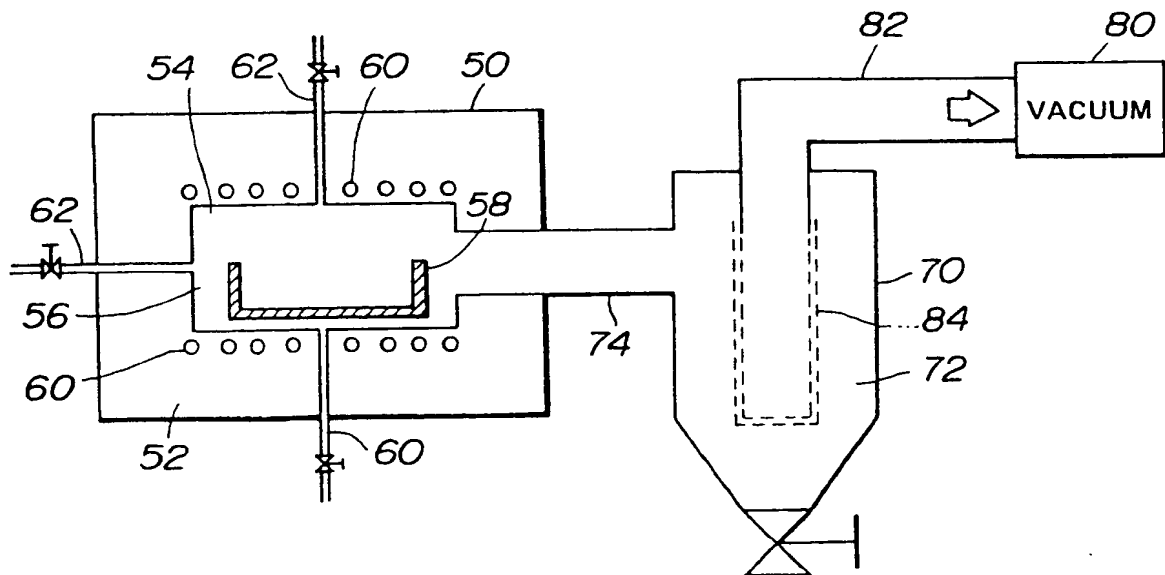
5 62. A system as set forth in claim 61, which is so arranged to place one of said carriage within said seventh means while the leading carriage stops within said second means.

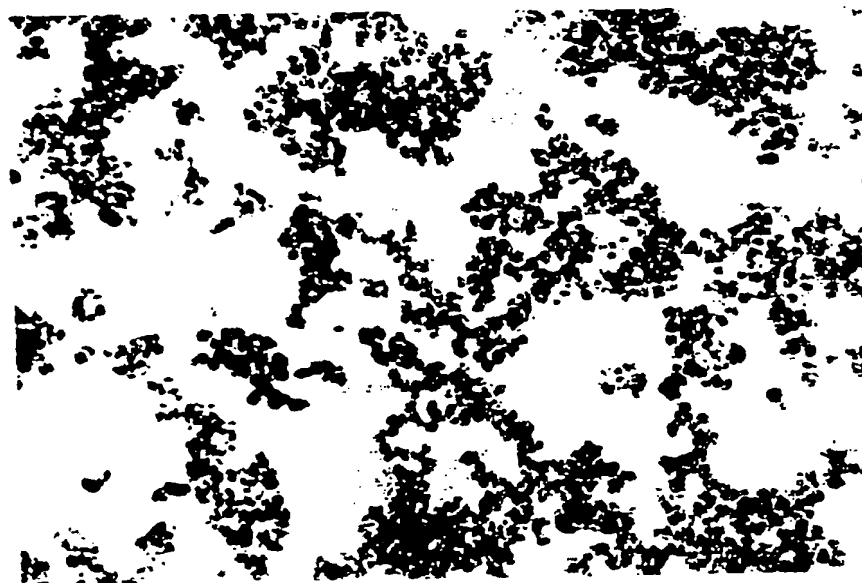
10 63. A system as set forth in claim 62, which is so arranged to place another carriages within said eighth means while the following carriage stops within said second means.

15 64. A system as sety forth in claim 48, wherein said seventh means, second means and said eighth means defines a continuous path for said material mixture, which path is filled with said material mixture and communicated with said first means for receiving continuous supply of said material mixture for causing  
20 travel of said material mixture within said path through said seventh, second and eighth means.

25 65. A system as set forth in claim 64, wherein said seventh, second and eighth means are aligned vertically.

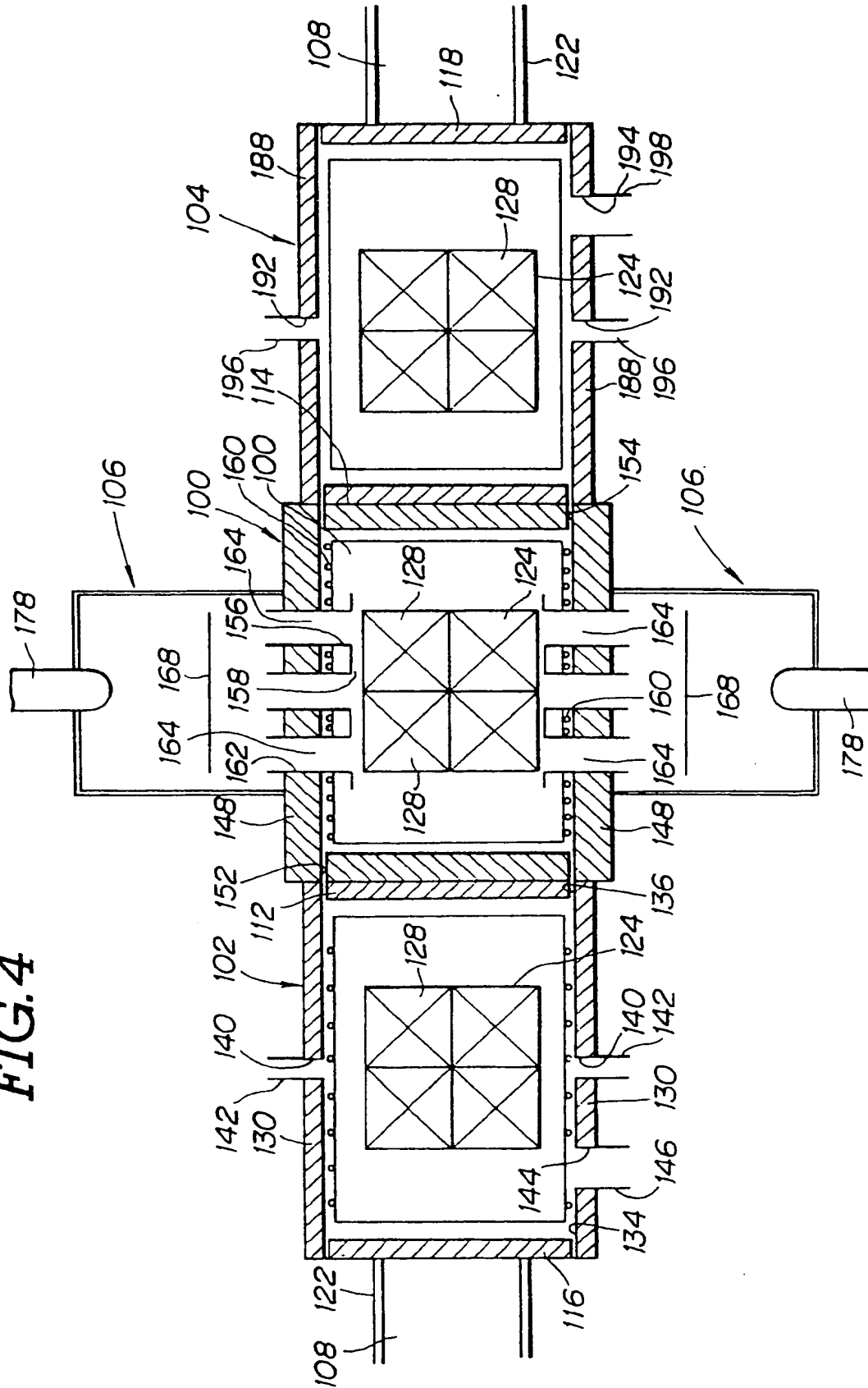
30 66. A system as set forth in claim 65, wherein first means comprises a hopper communicated with the top of said seventh means.

**FIG. 1****FIG. 2**

*FIG. 3*

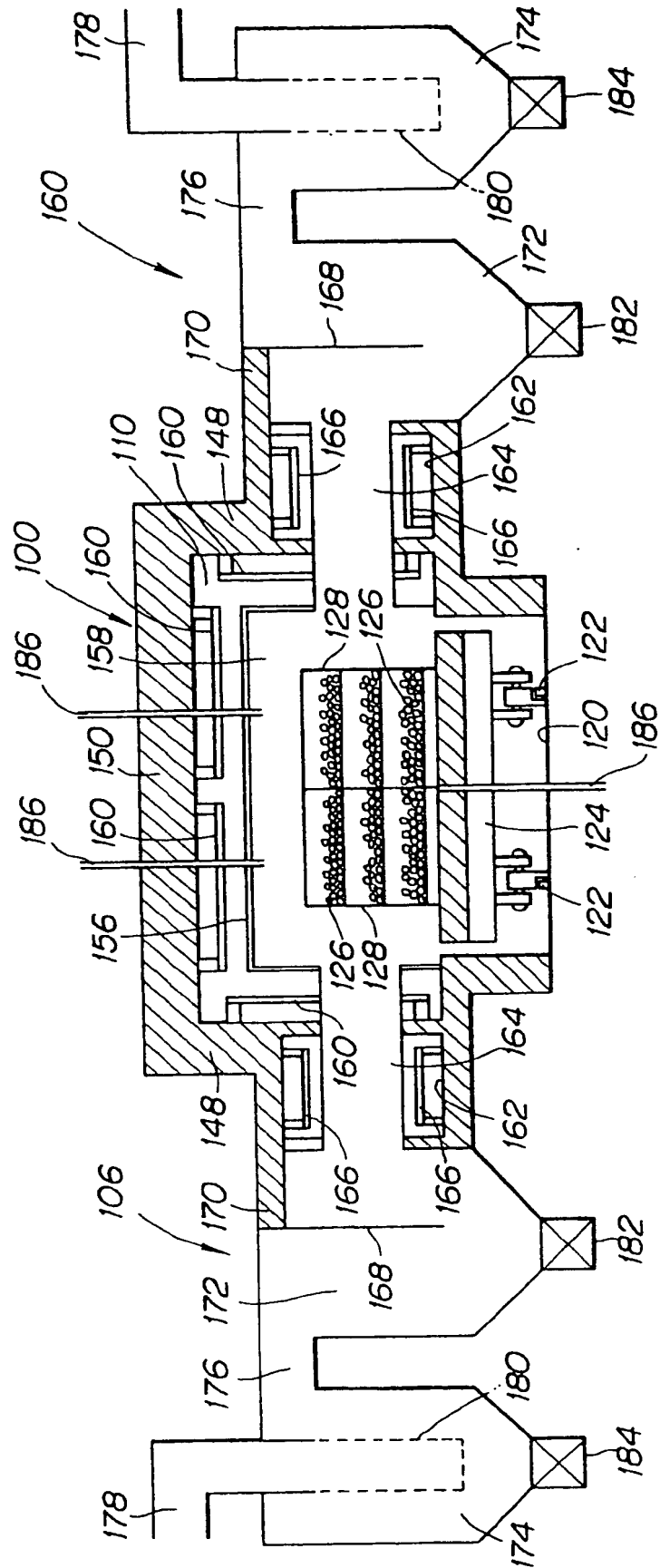
1000 Å

FIG. 4

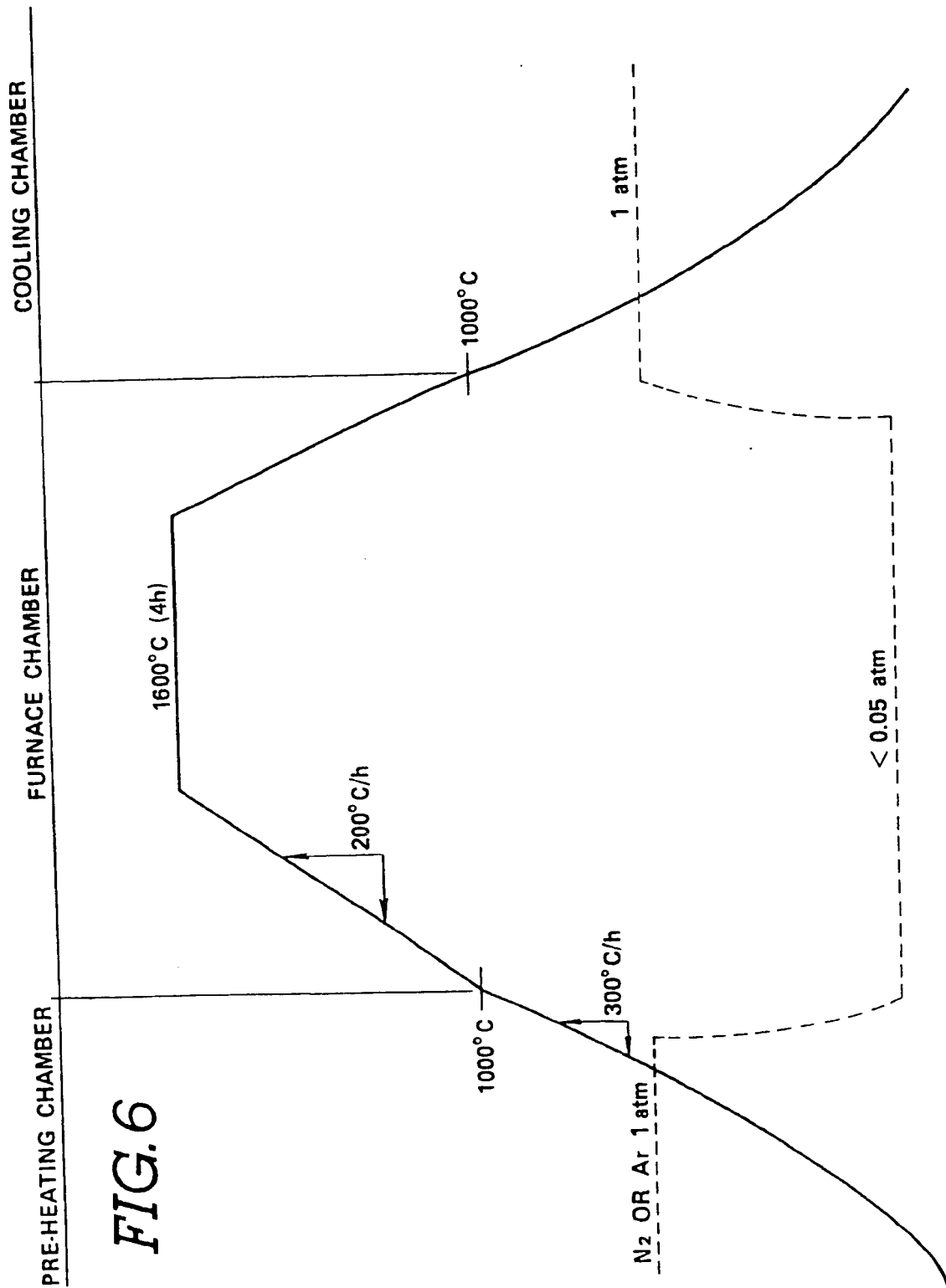


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FIG. 5

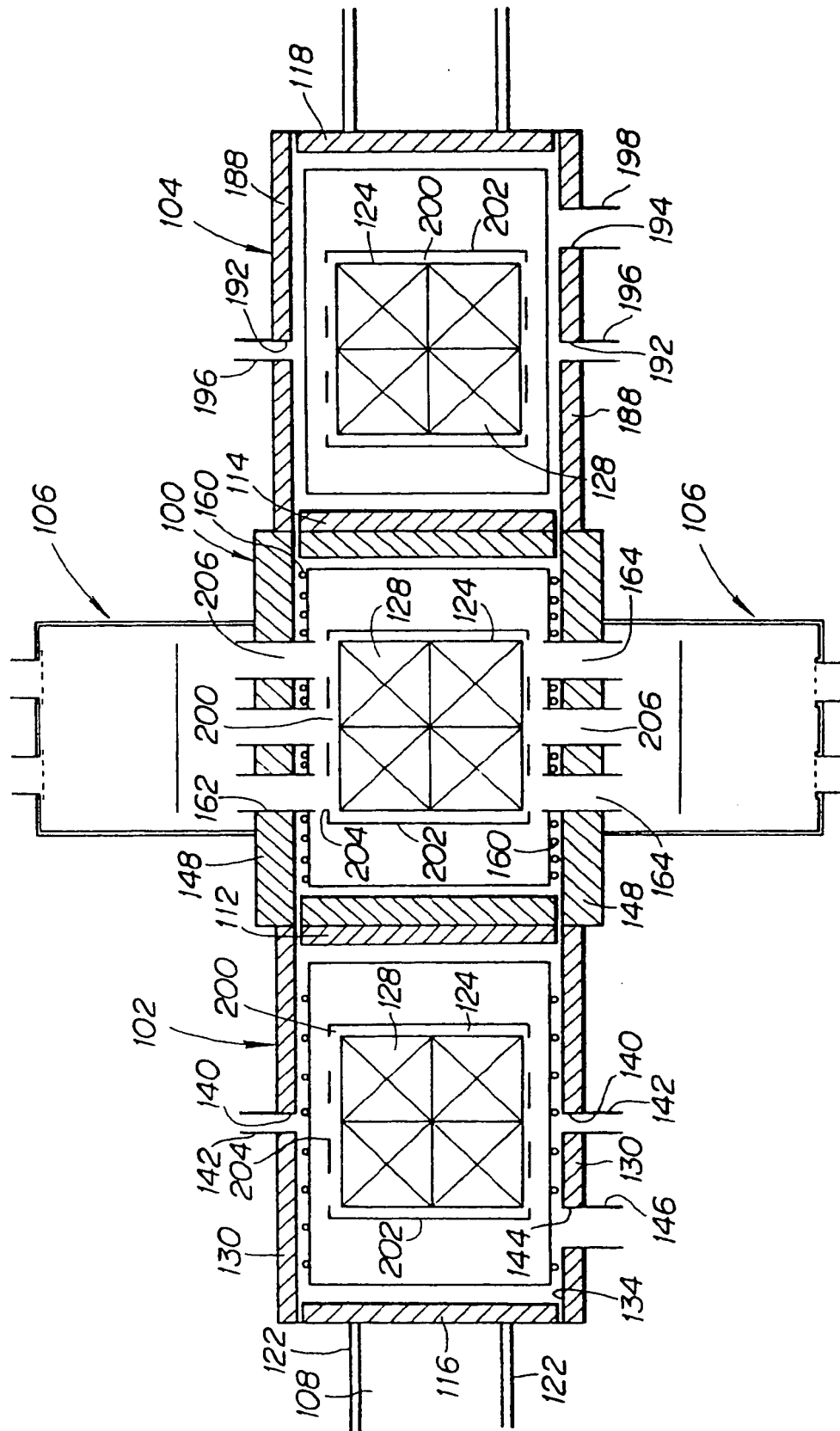


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FIG. 7





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FIG. 8

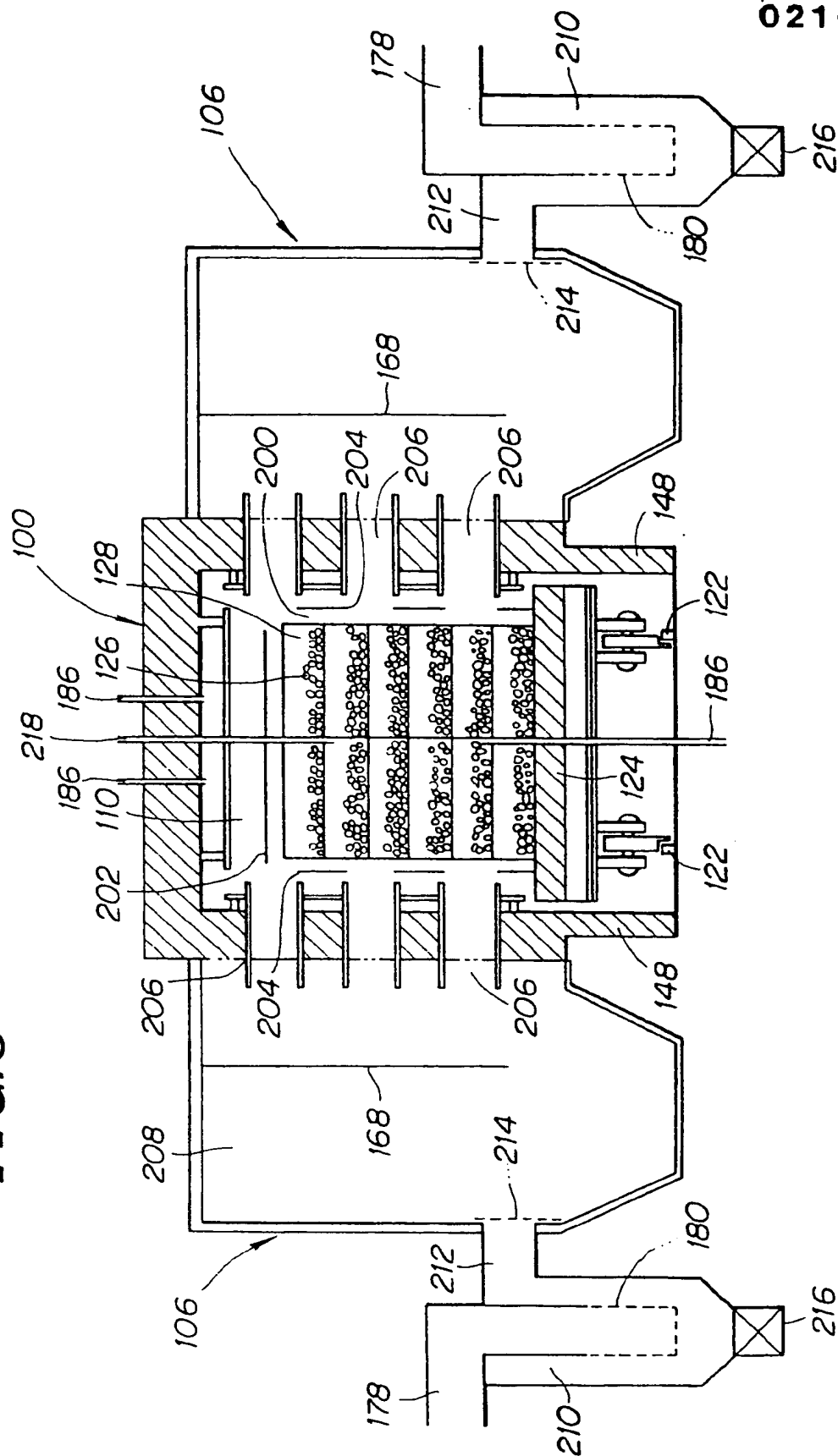
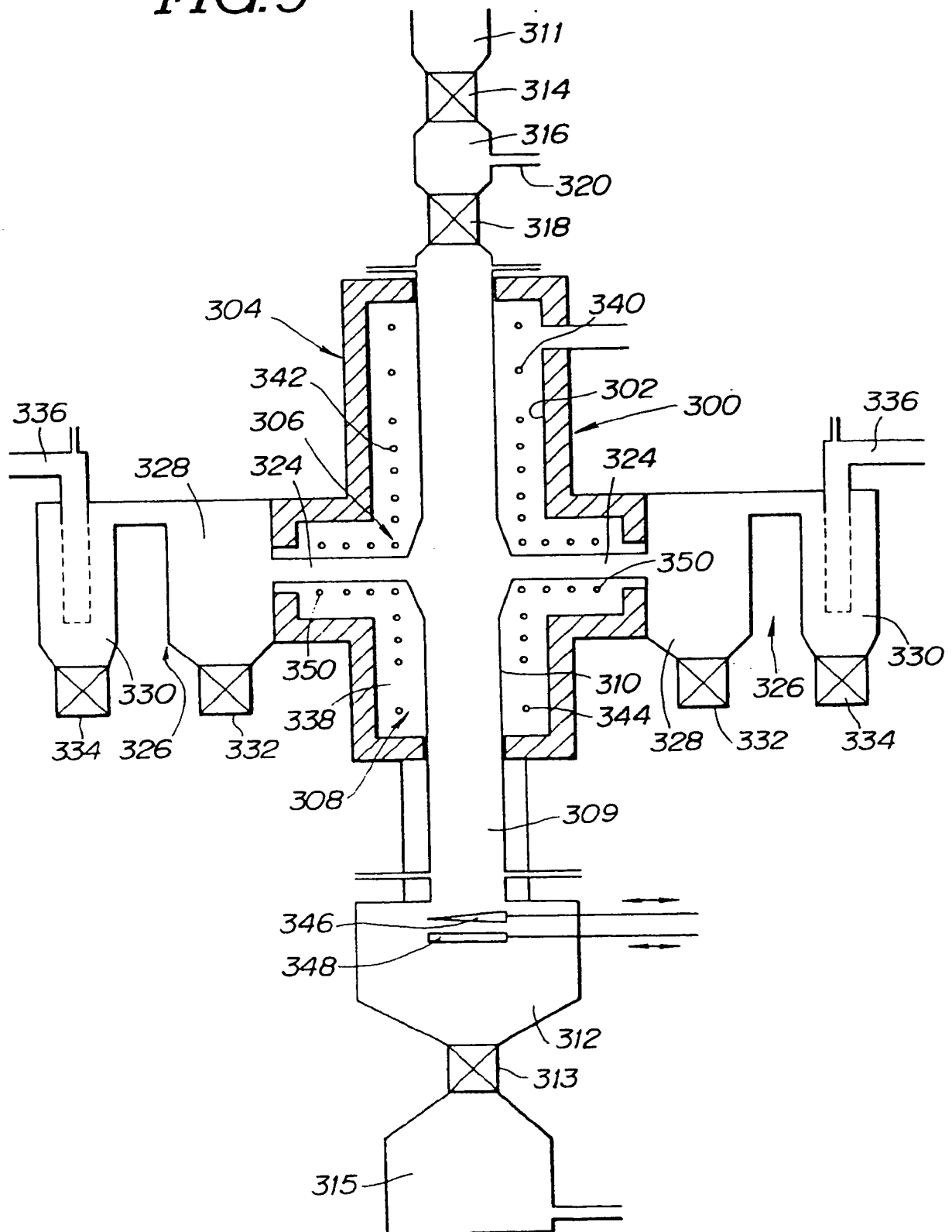


FIG. 9



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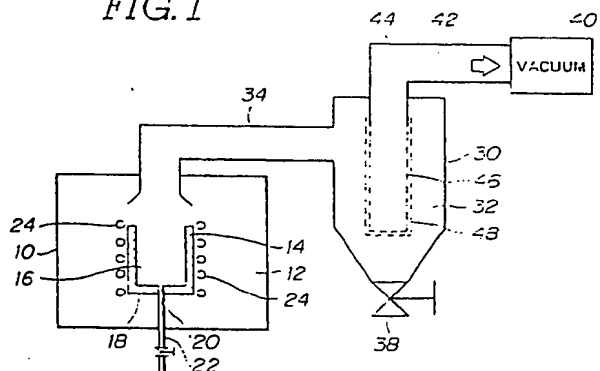
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64 Method and system for manufacturing fine-grained silicon monoxide.

57 A method and a device for manufacturing fine-grained SiO powder include a step (10) of heating a reagent mixture of SiO<sub>2</sub> containing material and Si and/or C containing material for generating SiO vapor, and a step (30) for condensing the generated SiO vapor in gaseous-state under the presence of non-oxidizing gas (22) and under substantially low pressure. Preferably, maintaining the atmosphere pressure at the position where thermal reaction to generate SiO vapor occurs at substantially low pressure, causes flow of the non-oxidizing gas. Such gas flow serves as transfer medium for transferring vapor-state SiO and/or fine-grained SiO powder to a SiO collection chamber. This successfully prevents the SiO from being accumulated within a transfer pipe or duct and thus preventing the pipe or duct from being blocked. Furthermore, substantially low pressure atmosphere encourages SiO vapor generation from the reagent mixture and thus requires lower heating temperature to cause SiO vapor generation.

FIG. 1





European Patent  
Office

# EUROPEAN SEARCH REPORT

Application Number

EP 86 40 1693

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	PATENT ABSTRACTS OF JAPAN, vol. 8, no. 85 (C-219)[1522], 18th April 1984; & JP-A-59 8613 (FUMIO HORI) 17-01-1984; & CHEMICAL ABSTRACTS, vol. 100, no. 24, June 1984, page 151, no. 194532b, Columbus, Ohio, US; & JP-A-59 08 613 (F. HORI) 17-01-1984; & JP-B-59 50 601 (Cat. D,A) ---	1	C 01 B 33/113 C 01 G 25/02 C 01 F 7/38 C 01 F 11/12 B 01 J 3/00 B 01 J 8/02 B 01 J 8/08
A	DE-A-2 139 446 (INSTITUT METALLURGII IMENI A.A. BAJKOWA AKADEMII NAUK SSSR) * Pages 13-14; example 2 * ---		
A	FR-A-1 132 075 (THE B.F. GOODRICH CO.) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 01 B 33/00
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 14-11-1988	Examiner BREBION J.CH.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	